HIGH RESOLUTION INFRARED SPECTRA OF AR-WATER AND NE-WATER AT 6 μm

Xunchen Liu Yunjie Xu*

Department of Chemistry
University of Alberta

67th International Symposium on Molecular Spectroscopy
June 20, 2012

Motivation to study Ar-H_2O

Prototypical system

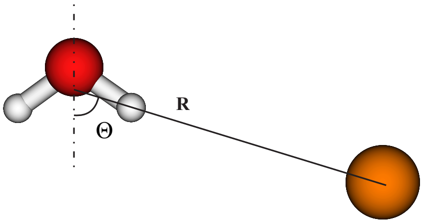
- Weak Interaction with Water
- vdW Potential Energy Surface
- Large Amplitude Motion

High resolution spectroscopy

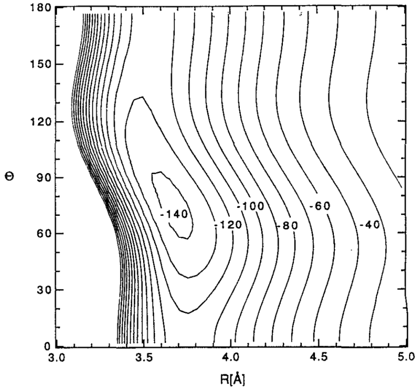
- Spectra measured in microwave, far-IR, near-IR, and mid-IR
- Some bands were missing from previous measurements
- Empirical PES still needs improvement comparing to *ab initio*

Structure of Ar-H_2O

- Planar T-shaped geometry
- Broad flat minimum, 143 cm^{-1}
- Large amplitude motion



Empirical AW2

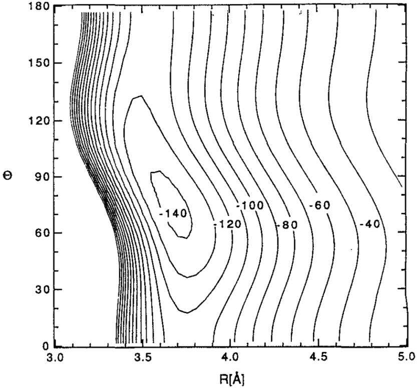


Cohen *et al.*, JCP, 98, 6007,**1991**.

PES of Ar-H_2O

Empirical AW2

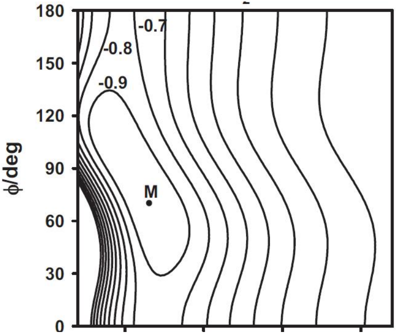
V_2=17.18 cm^{-1}



V_1=26.29 cm^{-1}

CCSD(T)/aug-cc-pVXZ/CBS

V_2=26.4 cm^{-1}



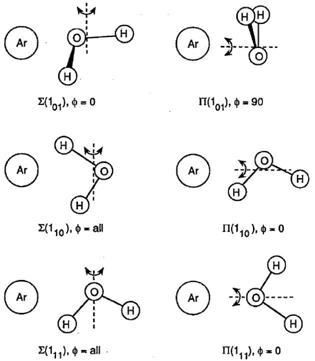
V_1=20.5 cm^{-1},

Makarewicz, JCP, 129, 184310,**2008**.

Hamiltonian

- H_2O vibration ($\nu_{1,2,3}$), van der Waals stretching (n)
- Nearly free internal rotation of H_2O correlates to $j_{k_a k_c}$
- Pseudo-diatomic end-over-end rotation (J, K)

$$\begin{aligned} H = \quad & G(\nu_{\mathrm{H_2O}}) + G(\nu_{\mathrm{vdW}}) \\ & +G(\nu_{\text{internal rotor}}) \\ & +B[J(J+1) - K] \\ & -D[J(J+1) - K]^2 \\ & +H[J(J+1) - K]^3 \end{aligned}$$

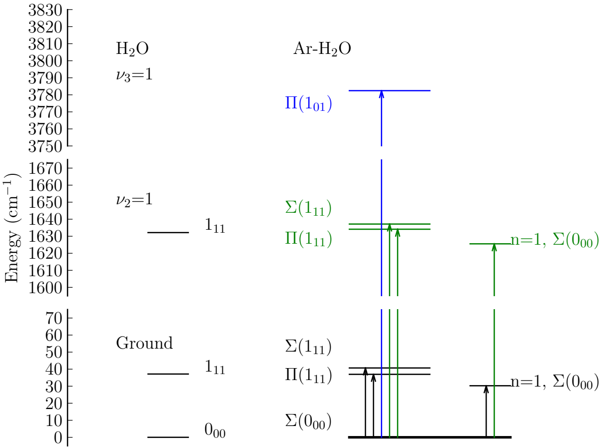


Coriolis Coupling

$$\begin{bmatrix} H_\Sigma & \beta\sqrt{J(J+1)} \\ \beta\sqrt{J(J+1)} & H_\Pi \end{bmatrix}$$

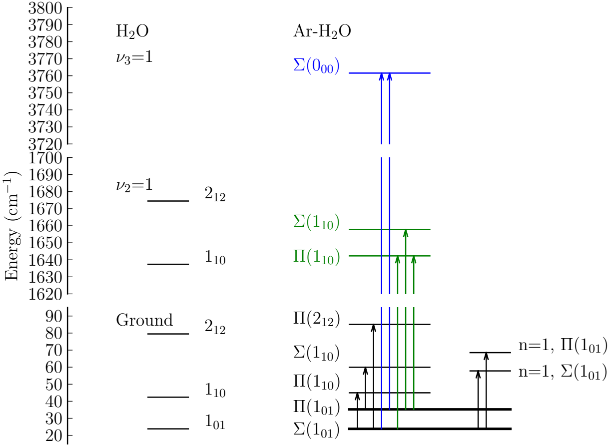
Hutson, JCP, 92, 157,**1990**. Cohen, Saykally, JCP, 95, 7891, **1991**. Weida, Nesbitt, JCP, 106, 3078, **1997**

Previous Measurements of para-H_2O-Ar



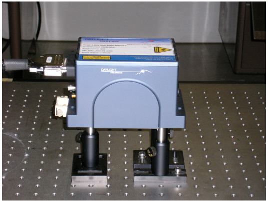
Cohen, Saykally, Ann.Rev.Phys.Chem, 42, 369, **1991** Nesbitt, Lascola, JCP, 97, 8096, **1997** Weida, Nesbitt, JCP, 106, 3078,

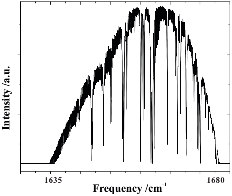
Previous Measurements of ortho-H_2O-Ar

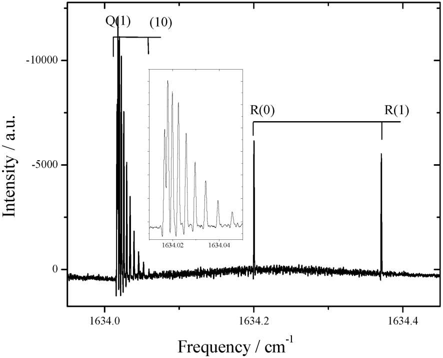


Cohen, Saykally, Ann.Rev.Phys.Chem, 42, 369, **1991** Lascola, Nesbitt, JCP, 95, 7917, **1997** Weida, Nesbitt, JCP, 106, 3078,

High Resolution mid-IR Spectrometer with an External-Cavity Quantum Cascade Laser







- continues-wave coverage up to 50 cm^{-1}, $< 0.001\,\mathrm{cm}^{-1}$ line width
- Multipass cell with rapid scan direct absorption method

UNIVERSITY OF ALBERTA

External-Cavity Quantum Cascade Laser (QCL)

Advantage:

High output power affords the usage of a larger number of multipass
Continuous (mode hop free) tuning range cover over 50 cm-1

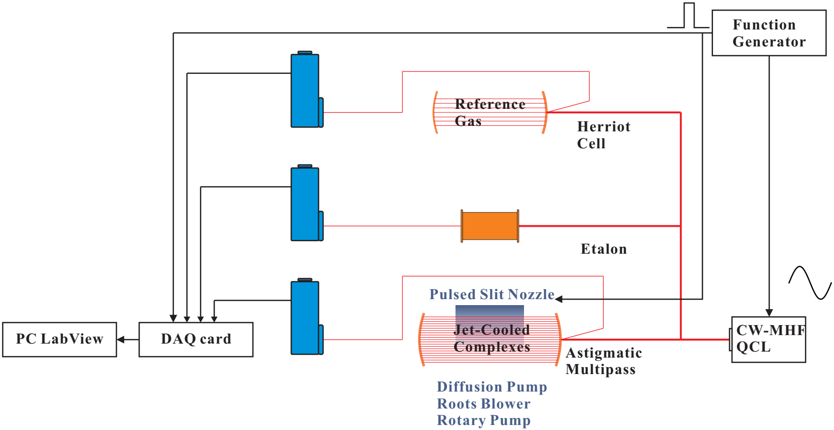
Limitation:

Scan rate $\leq$100 Hz limits the sensitivity
Small shift in subsequent laser scans limits resolution

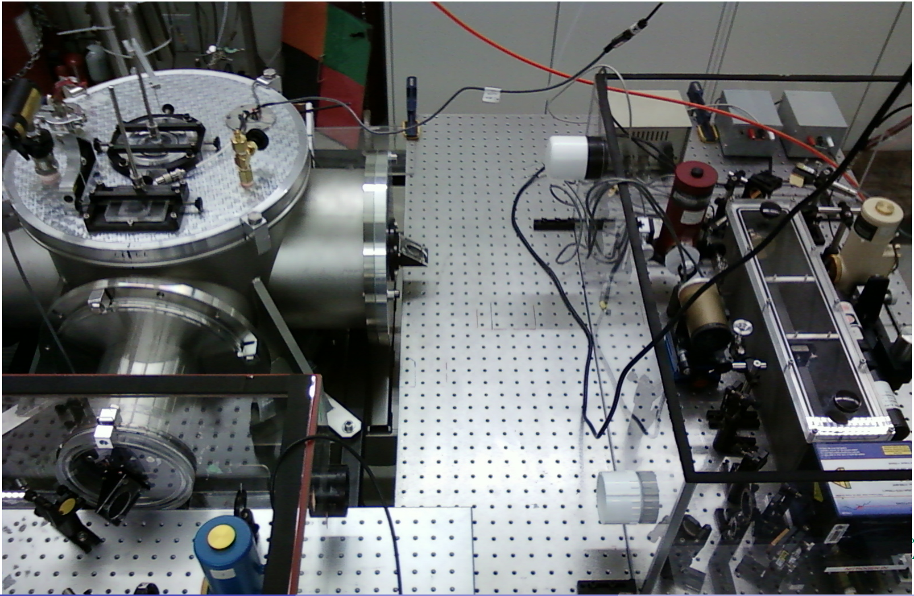
On-the-fly calibration

Simultaneous measurements of jet, reference and etalon channels
Frequency calibration with HITRAN08 for each scan before averaging

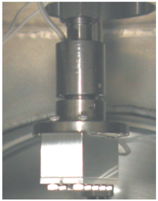
Spectrometer Overview

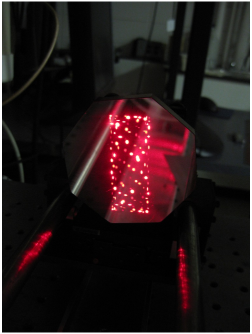
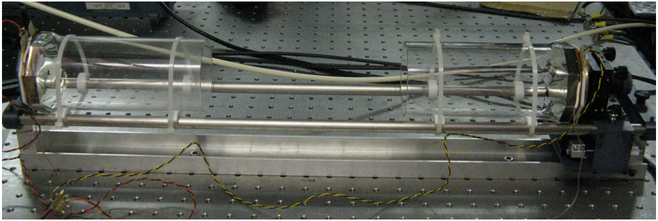


Spectrometer Overview



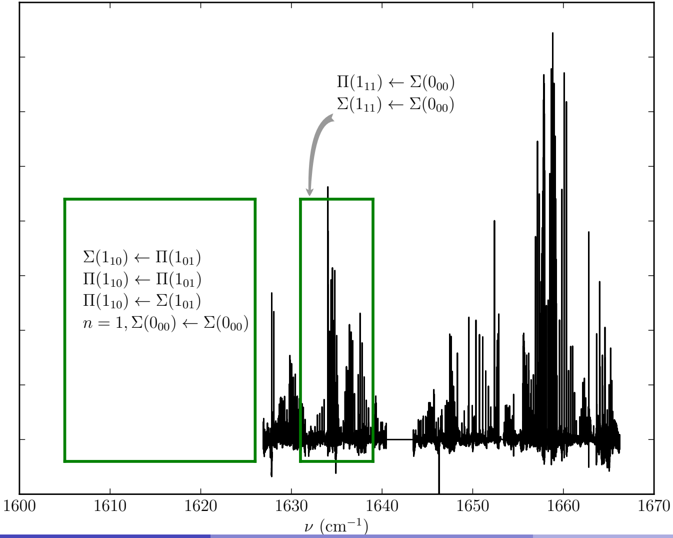
Homemade Slit Nozzle
Astigmatic Multi-Pass Cell



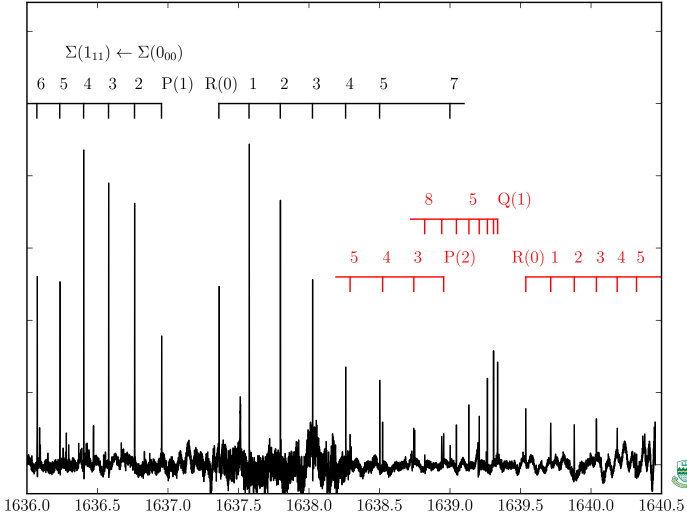



- two 25 μm 4 cm slit nozzles
- 3" astigmatic mirror aligned to 366-pass allowd by high power from QCL
- 0.2% H_2O, 4% Ar in 10 ktorr Ne backing gas

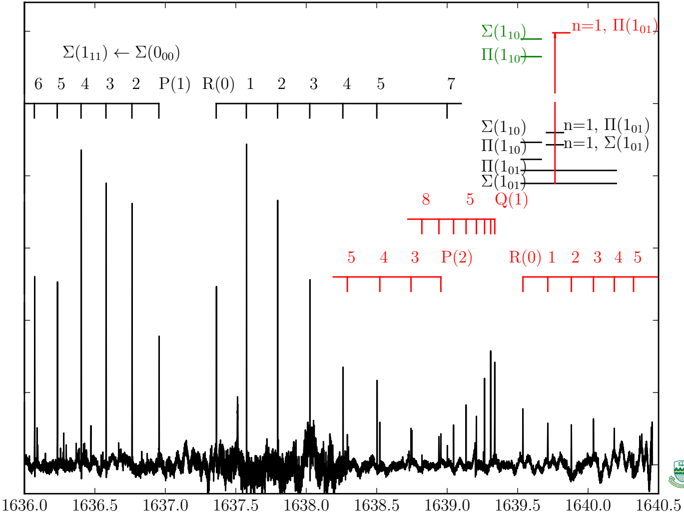
Overview of Ar-H_2O spectrum



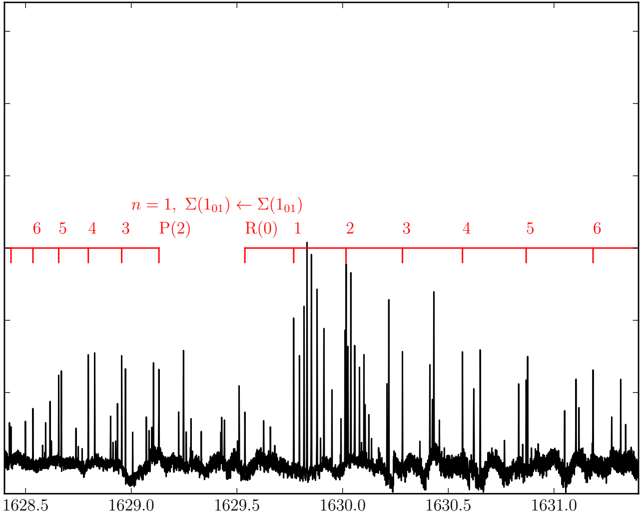
$n = 1, \Pi(1_{01}) \leftarrow \Sigma(1_{01})$



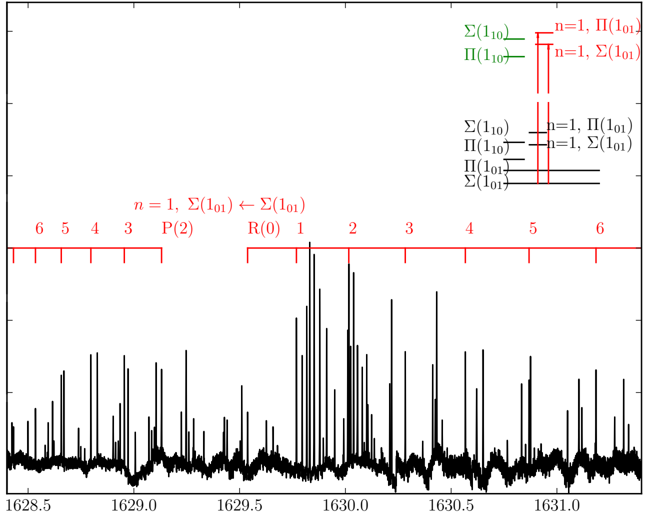
$n = 1, \Pi(1_{01}) \leftarrow \Sigma(1_{01})$



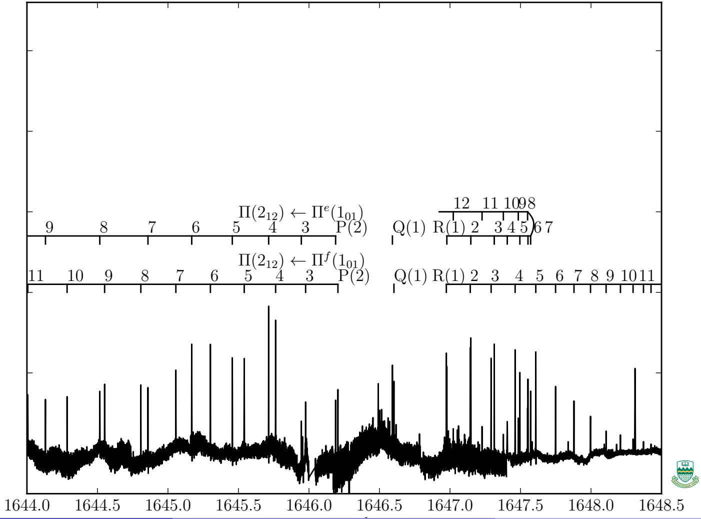
$n = 1, \Sigma(1_{01}) \leftarrow \Sigma(1_{01})$



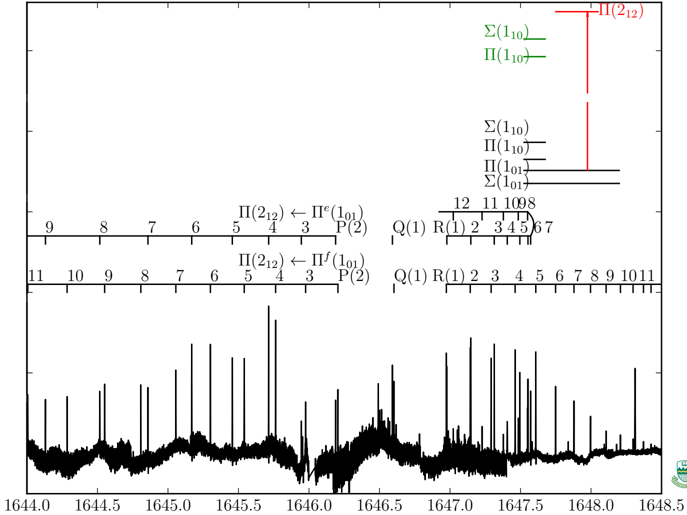
$n = 1, \Sigma(1_{01}) \leftarrow \Sigma(1_{01})$



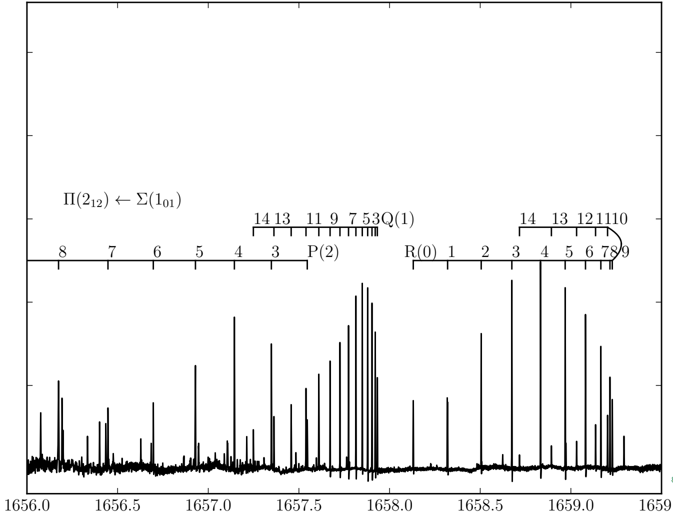
$\Pi(2_{12}) \leftarrow \Pi(1_{01})$



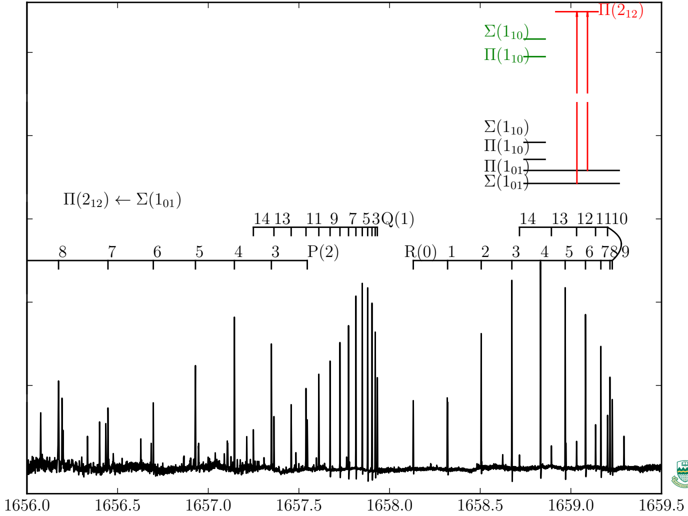
$\Pi(2_{12}) \leftarrow \Pi(1_{01})$



$\Pi(2_{12}) \leftarrow \Sigma(1_{01})$

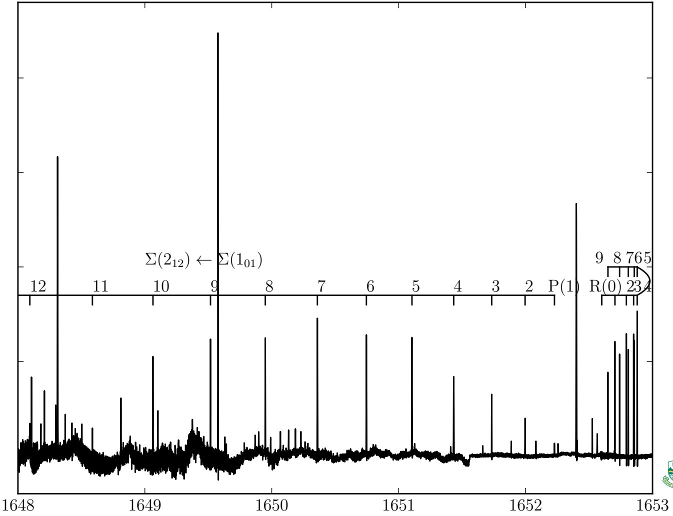


$\Pi(2_{12}) \leftarrow \Sigma(1_{01})$

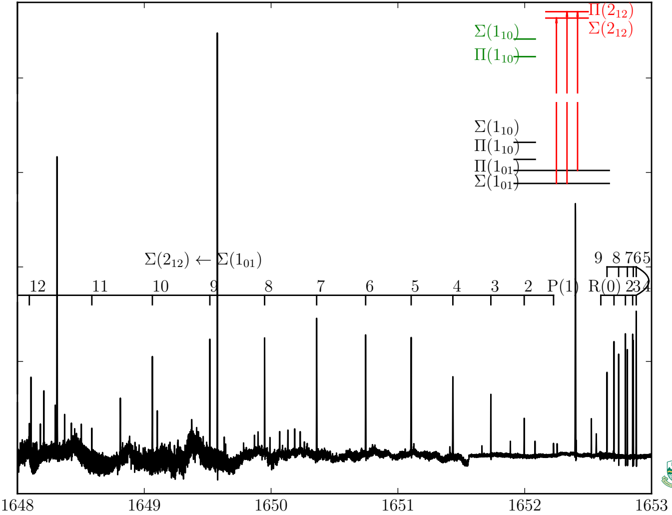


UNIVERSITY OF ALBERTA

$\Sigma(2_{12}) \leftarrow \Sigma(1_{01})$



$\Sigma(2_{12}) \leftarrow \Sigma(1_{01})$

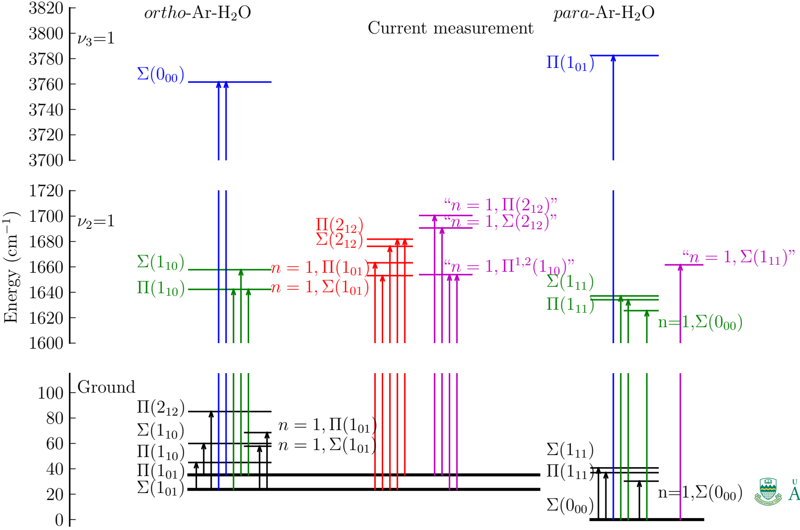


Spectroscopic Constants

	$\nu(cm^{-1})$	B(MHz)	D(kHz)	H(Hz)
v_2=1				
$\Sigma^e(2_{12})$	1652.4213(7)	2422.6(19)	-727(32)	-1798(166)
$\Pi^e_f(2_{12})$	1658.0307(6)	2831.03(55)	1593(15) 142.3(29)	2569(55) 0^a
β(MHz)	2799(30)			
v_2=1,n=1				
$\Sigma^e(1_{01})$	1629.3257(7)	3259.7(42)	-413(134)	-4640(1280)
$\Pi^e_f(1_{01})$	1639.4422(6)	2696.2(16)	345(71) 140(24)	0^a 0^a
β(MHz)	4985(66)			

[a] Zero within uncertainty, and set to zero in final fit.

H_2O-Ar levels (ambiguous bands correct to abstract)



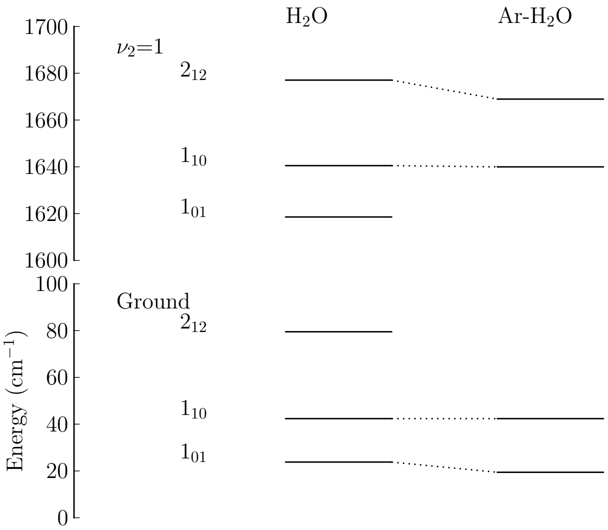
Splitting of the internal rotor states

	n=0	n=1
Ground		
1_{01}	11.428610	10.729896
1_{10}	14.983385	
v_2=1		
1_{01}		10.1165
1_{10}	15.4845	
2_{12}	5.6094	

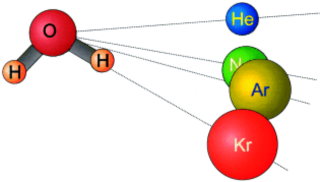
- $\Sigma(2_{12})$ level is shifted down by $10\,\mathrm{cm}^{-1}$?
- coupling with another level?

UNIVERSITY OF ALBERTA

H_2O-Ar internal rotor states (average of Σ/Π levels)



Rg-H_2O vdW interaction



MRCI
Aquilanti et al. *Angew. Chem. Int. Ed.* 44, 2356, **2005**.

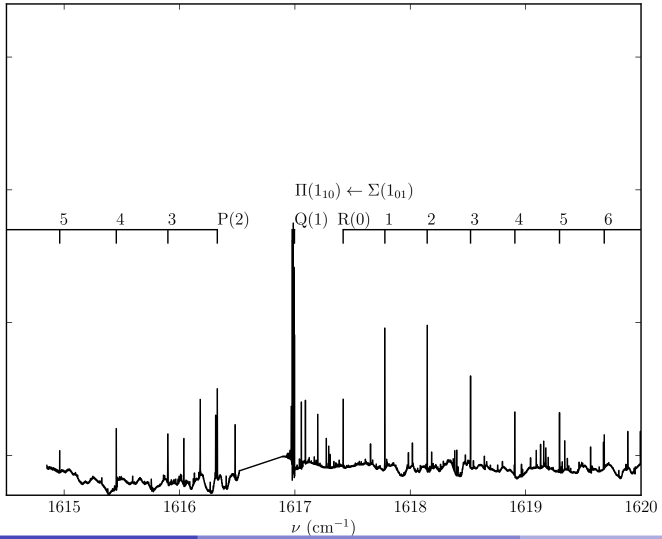
	binding energies (cm^{-1})
He-H_2O	34.74
Ne-H_2O	64.89
Ar-H_2O	140.9
Kr-H_2O	167.6

CCSD(T)/aug-cc-pVXZ/CBX
Makarewicz, JCP, 129, 184310,**2008**.

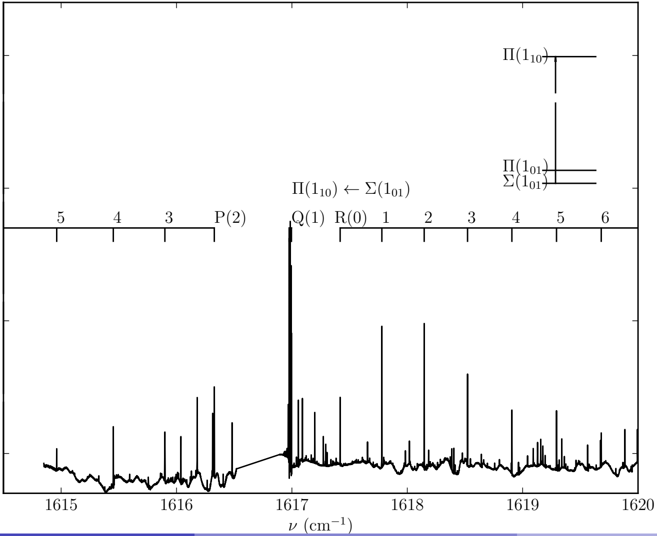
Ne-H_2O

- Shallower PES leads to fewer bound internal rotor states and stronger rovibrational coupling
- High resolution spectrum of Ne-H_2O had not been observed
- Ne-D_2O spectra have observed in the v_2=1 region:
  $\Pi(1_{11}) \leftarrow \Sigma(0_{00})$, $\Sigma(1_{11}) \leftarrow \Sigma(0_{00})$,
  $n = 1, \Sigma(0_{00}) \leftarrow \Sigma(0_{00})$
  Song *et al.* JCP, 135, 134304, **2011**.
- We observed Ne-H_2O bands in close proximity of Ar-H_2O bands

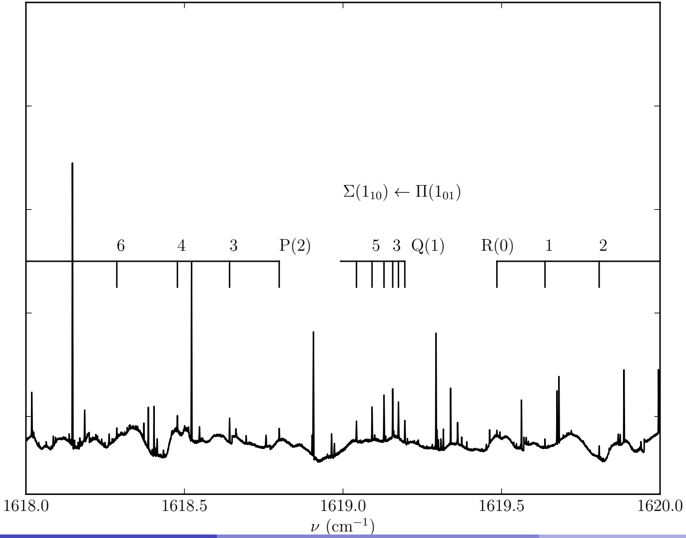
$\Pi(1_{10}) \leftarrow \Sigma(1_{01})$



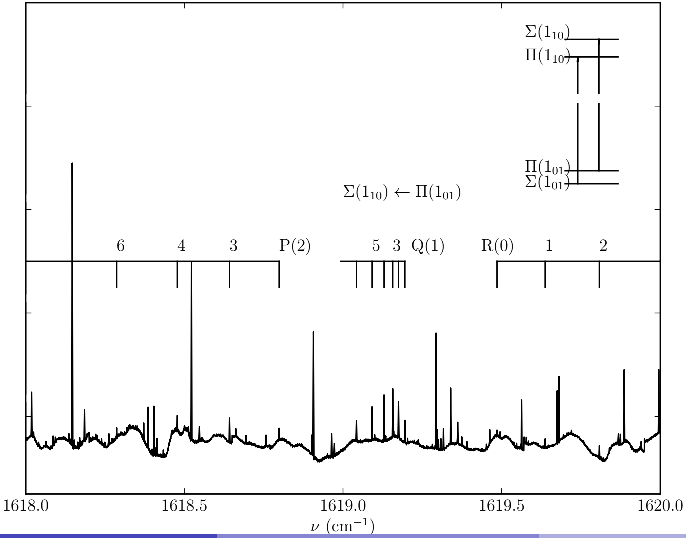
$\Pi(1_{10}) \leftarrow \Sigma(1_{01})$



$\Sigma(1_{10}) \leftarrow \Pi(1_{01})$

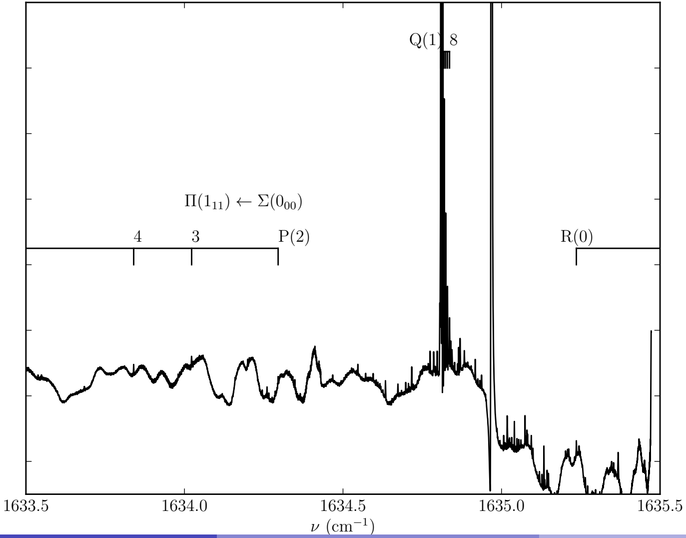


$\Sigma(1_{10}) \leftarrow \Pi(1_{01})$

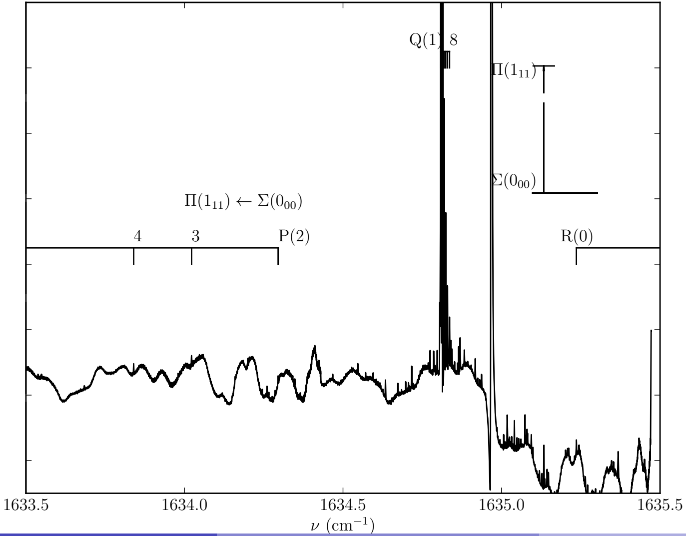


UNIVERSITY OF ALBERTA

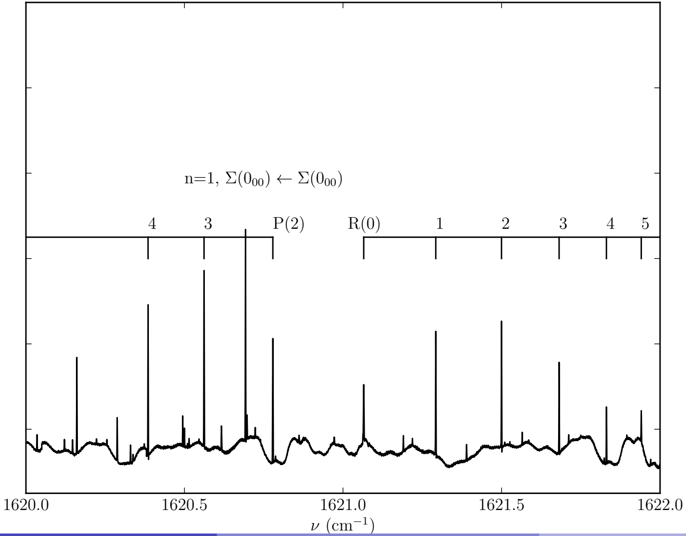
$\Pi(1_{11}) \leftarrow \Sigma(0_{00})$



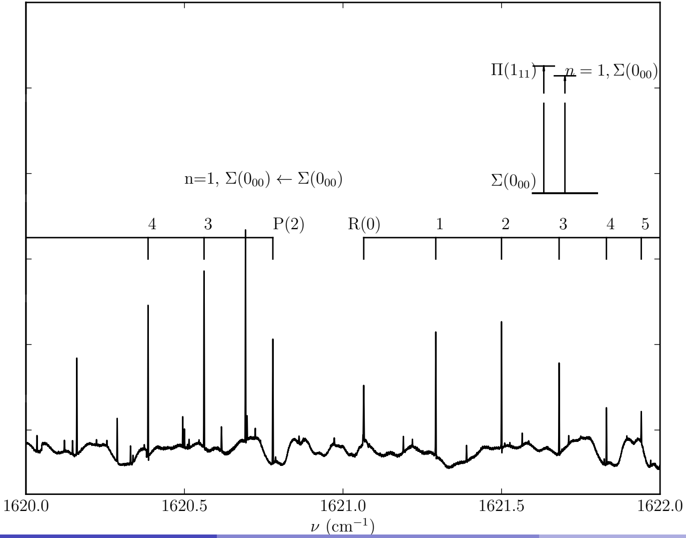
$\Pi(1_{11}) \leftarrow \Sigma(0_{00})$



$n = 1, \Sigma(0_{00}) \leftarrow \Sigma(0_{00})$



$n = 1, \Sigma(0_{00}) \leftarrow \Sigma(0_{00})$



He-H_2O

Experiment

No absorption feature of He-H_2O was observed in our experiment

Theory

D_e=34.74 cm^{-1}, D_0=6.90 cm^{-1}
The only bound internal rotor state: $\Sigma 0_{00}$ with J=0-4
Wang, Carrington Jr, CSTC, 2010

UNIVERSITY OF ALBERTA

Summary

Ar-H_2O

- 5 new bands of vdw stretching and 2_{12} internal rotor states unambiguously assigned
- 5 ambiguously assigned bands indicating new internal rotor states
- strong Coriolis coupling and radial-angular coupling

Ne-H_2O

- *ortho*-Ne-H_2O: $\Sigma(1_{10}) \leftarrow \Pi(1_{01})$, $\Pi(1_{10}) \leftarrow \Sigma(1_{01})$
- *para*-Ne-H_2O: $n = 1, \Sigma(0_{00}) \leftarrow \Sigma(0_{00})$, $\Pi(1_{11}) \leftarrow \Sigma(0_{00})$

Acknowledgment

Dr. Yunjie Xu research group
Dr. Wolfgang Jäger research group

NSERC CRSNG

Canada Foundation for Innovation
Fondation canadienne pour l'innovation

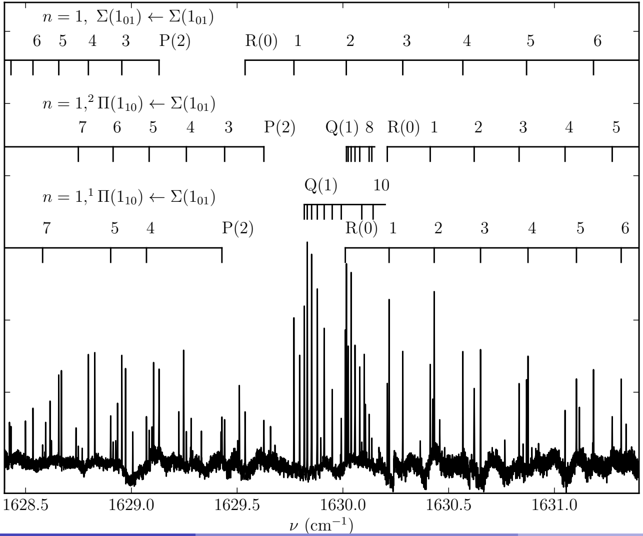
Alberta Innovates Technology Futures

BMO

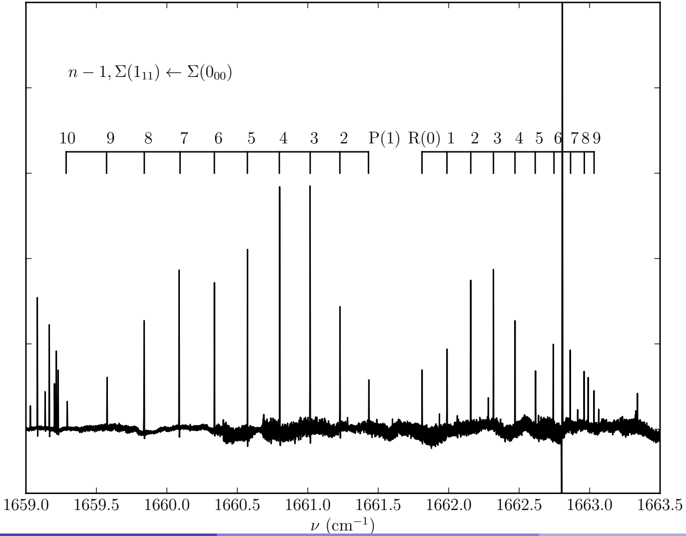
UNIVERSITY OF ALBERTA

Thanks for your attention!

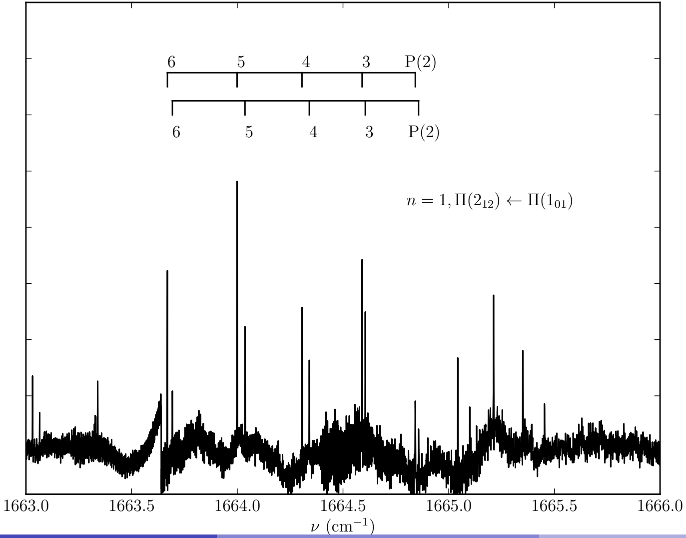
$n = 1, \Sigma(1_{01}) \leftarrow \Sigma(1_{01})$



$n = 1, \Sigma(1_{11}) \leftarrow \Sigma(0_{00})$



$n = 1, \Pi(2_{12}) \leftarrow \Pi(1_{10})$



$n = 1, \Sigma(2_{12}) \leftarrow \Pi(1_{10})$